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Application of optical, chemical and thermal methods to the analysis of inorganic and organic constituents in phosphatic pellets (Tunisia)

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A study of “pellets”, phosphatic grains whose size lie between 50 and 200 μm , of the Tertiary Gafsa Metlaoui basin (Tunisia) has been performed by X-ray diffraction, IR spectroscopy, CNS elementary analysis, microscopy (photonic, conventional MEB and Cryo-MEB), Rock-Eval analysis.

The X-ray diffraction shows that the fundamental mineral within these phosphatic pellets is “carbonate-fluorapatite” or “francolite”.

This francolite is characterized by low values of its cell parameters a and c : the a parameter is comprised between 9.291 and 9.322 Å and the c parameter between 6.874 to 6.899 Å. The comparison with other natural and synthetic similar apatitic compounds (francolite and fluorapatite) shows isomorphic substitutions in the crystal lattice of the pellets francolite and, in particular, the introduction of carbonate ions into the crystal lattice. This substitution of ions PO_4^{3-} by ions CO_3^{2-} is confirmed by the infra-red spectroscopy which shows low contents of CO_2 (from 2.75 to 3.82% of total sites), i.e. a carbonate fluorapatite of the type B (Benalioulhaj, 1989).

Mineralogical and chemical studies let us to establish a structural formula for an apatite within a studied sample as: $(\text{Ca}_{4,63} \text{Mg}_{0,13} \text{Na}_{0,22}) ((\text{PO}_4)_{2,51} (\text{CO}_3)_{0,48}) (\text{OH}_{0,77} \text{F}_{0,23})$.

Observations under conventional MEB show a characteristic hexagonal shape for apatite minerals. Detailed examination of these minerals shows that each large mineral is formed by smaller hexagonal crystals (lower than $1\mu\text{m}$ in larger dimension). In certain cases, we observed, between the apatite microcrystals, stick forms with a median contraction, suggesting bacterial bodies.

In pellets, carbon is divided into organic and mineral carbon. Knowing the values of total carbon by LECO-2000 analysis, it was possible to obtain the mineral carbon content by

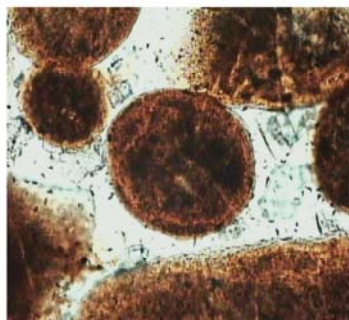
deducing the organic carbon content from the total organic content. The organic carbon content varies within pellets from 0.11 to 1.74 %.

The organic matter appears as constituted by tangled filaments binding apatite crystallites. The observation in Cryo-MEB gives evidence of the presence of filamentous, intrapelletal, organic matter.

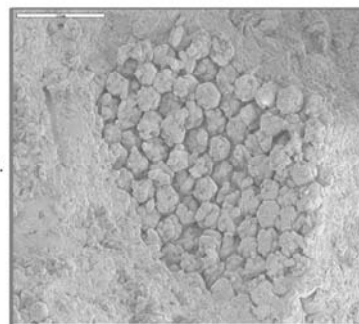
The study of the organic matter with Rock-Eval VI pyrolysis confirmed the origin of the organic matter associated with phosphatic pellets, i.e. its marine planktonic origin (Belayouni et Trichet, 1983, Nathan, 1990)

Interestingly, the Rock-Eval technique allows the distinction of the CO₂ liberated by the pyrolysis of the intrapelletal organic matter from the CO₂ produced during the thermal cracking of the carbonate-fluorapatite.

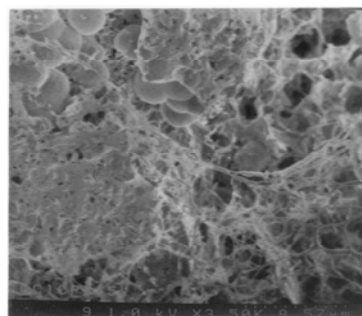
In addition, it leads to the following fundamental result: values of HI, OI and Tmax confirm the humic (i.e. very poorly evolved in the range of diagenesis as well as from a thermal point of view) character of the organic matter contained in pellets. This character is typical of an organic matter which has been entrapped in a mineral (apatitic) network and whose diagenetic evolution has been empeached. Let us recall that the Tunisian phosphatic ores are Early Tertiary in age and that the presence of a humic organic matter within the pellets is in contradiction with such an age as well as with the kerogen nature of the organic matter within the sedimentary matrix embedding the pellets. As such apatite and its associated organic matter constitute a typical "organo-mineral" association.



Section of phosphatic grains embedded in micritic cement, observed under Reflected Light. Mean diameter of the central grain is 200 μm



Fractured surface of a phosphatic pellet, observed under SEM, showing crystallised apatite



Fractured surface of a phosphatic pellet, apatite dissolved by HCl, observed under SEM, and showing intrapelletal organic matter

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